High Pressure-Assisted Synthesis of 1,2,3-Trialkyldiaziridines from N-Chloroalkylamines

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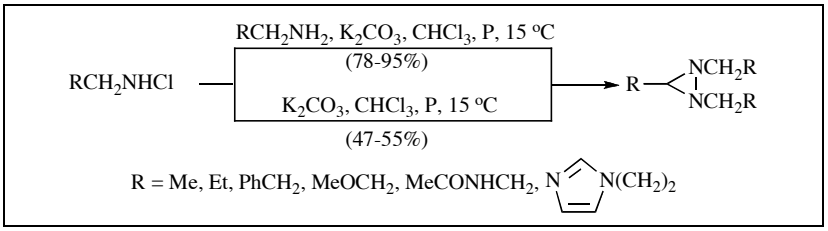

New method for the preparation of 1,2,3-trialkyldiaziridines **1** in high yields, based on the transformation of *N*-chloroalkylamines **3** without using carbonyl compounds in the presence of primary aliphatic amines with the same alkyl fragment, potassium carbonate and a small amount of water in $CHCl_3$ under high pressure (500 MPa), was developed. Diaziridines **1** can be synthesized in the same conditions using a larger amount of potassium carbonate instead of primary aliphatic amines however in lower yields. The kinetic investigations on the synthesis of 1,2-diethyl-3-methyldiaziridine **1a** from *N*-chloroethylamine **3a** have shown that the reaction leading to diaziridine **1a** proceeds according to the law of the second order.

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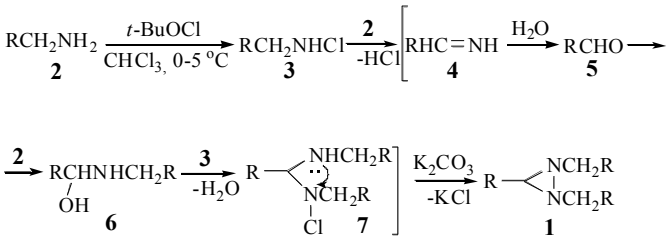
INTRODUCTION

In recent years we have been interested in developing optimal approaches to the synthesis of differently substituted diaziridines from carbonyl compounds, primary aliphatic amines and aminating reagents (in paticular *N*-chloroalkylamines) [1-5]. These studies were motivated by a few reasons. First, diaziridines displayed psychotropic activity [6-9]. In addition, they include configurationally stable nitrogen atoms under normal conditions and thereby are usable for investigations of nitrogen stereochemistry [10-12]. And finally they may enter ring expansion reactions with electrophilic reagents given a heightened tensity of the three-member ring [13,14]. Our recent investigations of the transformations of 1,2-di-, 1,2,3-tri- and 1,2,3,3-tetraalkyldiaziridines and their bi-cyclic analogs 1,5-diazabicyclo[3.1.0]hexanes under the action of heterocumulenes (ketenes, isocyanates and isothiocyanates) resulted in new simple methods for the synthesis of both known and new heterocyclic systems [15-19]. Therefore, a search for new methods for the preparation of diaziridines retains its relevance.

Earlier [3], while examining the ways of optimizing of the methods for the synthesis of 1,2-di and 1,2,3-trialkyl-diaziridines **1** from carbonyl compounds, primary aliphatic amines **2** and *N*-chloroalkylamines **3**, we studied the behavior of *N*-chloroalkylamines **3** in the presence of amine **2** in excess and (or) inorganic bases in chloroorganic solvents. Unexpectedly, it was found out that a reaction of *N*-chloroalkylamines **3** with primary aliphatic amines **2**, containing the same alkyl fragment, in the absence of carbonyl compounds and in the presence of potassium carbonate and a small water amount at room temperature resulted in 1,2,3-trialkyldiaziridines **1** where 3-alkyl fragments contained one CH_2-group less than the alkyl fragment of the initial compounds. Proceeding from the structure of the obtained products we assumed that the first step of this reaction should be the conversion of *N*-chloroalkylamines **3** into aldimines **4** as a result of HCl E_2-elimination in the presence of amines **2**. Compounds **4** are hydrolyzed to aldehydes **5** in the presence of water by analogy with reactions reported in reference [20]. In according to known data [21,3,4] it was assumed that a carbonyl compounds **5** and an amines **2** were condensed into α-aminocarbinols **6**, which underwent α-amino-alkilation of N-chloroamines **3** to give *N*-chloroaminals **7**; the latter underwent cyclization into diaziridines **1** due to S_n^i process in the presence of a base (Scheme 1). However a low velocity of this reaction impedes its application. For aliphatic *N*-chloroalkylamines **3**, the reaction ended only in several days, and for *N*-chloroalkylamines **3** synthesized from amines **2** with lower basicity lasted for several weeks. Anyhow the variant for the synthesis of diaziridines **1** could be useful in the cases where carbonyl compounds were less accessible than corresponding amines **2**.

The specific goal of this research was to develop a new approach to the preparation of 1,2,3-trialkyldiaziridines **1** on the basis of the transformation of *N*-chloroalkylamines **3** in the absence of carbonyl compounds using high pressure methods.

Scheme 1



RESULTS AND DISCUSSION

At the first step of the research, we looked to the regularity of the disappearance of *N*-chloroalkylamines **3** and accumulation of diaziridines **1** in time using the NMR method ($CDCl_3$, δ, ppm). For that, we examined a possibility of preparing 1,2-diethyl-3-methyldiaziridine **1a** from *N*-chloroethylamine **3a** and ethylamine **2a** (molar ratio 1:3) in the presence of potassium carbonate and the trace water amount at atmospheric pressure and room temperature. The reaction ran controlled through detecting the disappearance of more characteristic signals of *N*-chloroethylamine **3a** protons (Cl-*N*-CH_2, t, 2.85) and arising of diaziridine **1a** protons ($MeC^3_{diaz.\ ring}$, d, 1.22 and Me*CH*-$N_{diazir.\ ring}$, m, 2.12). The regularity of the change in the concentrations of *N*-chloroethylamine **3a** and diaziridine **1a** in time is shown in Figure 1.

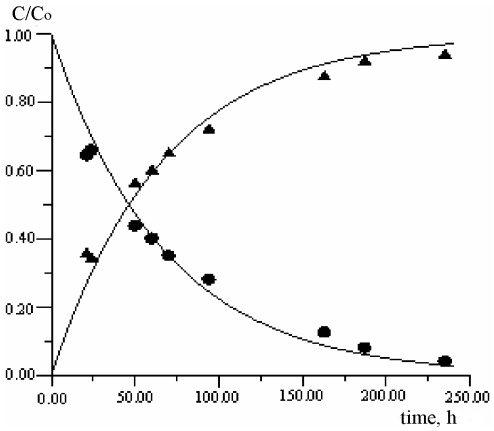


Figure 1. Regularities of the *N*-chloroethylamine **3a** disappearance (●) and the 1,2-diethyl-3-methyldiaziridines **1a** accumulation (▲) in time at atmospheric pressure.

The experimental data match the curves built according to the second order law (Equations 1 and 2).

$$-\frac{d[C_{ax}]}{dt} = \frac{d[C_D]}{dt} = k[C_{AX}][C_A] \qquad (1)$$

$$[C_{AX}] = \frac{[C_{AX}]_0([C_A]_0 - [C_{AX}]_0)}{[C_A]_0 \exp^{k([C_A]_0 - [C_{AX}]_0)t} - [C_{AX}]_0} \qquad (2)$$

Where $[C_{AX}]_0$, $[C_A]_0$, $[C_D]_0$, $[C_{AX}]$, $[C_A]$, $[C_D]$ – initial and current concentrations of *N*-chloroethylamine **3a**, ethylamine **2a** and diaziridine **1a**, accordingly; $[C_D]=[C_{AX}]_0 - [C_{AX}]$. The obtained kinetic data allow the assumption that the limiting step of the process is a bimolecular reaction of *N*-chloroethylamine **3a** with ethylamine **2a** followed by the elimination of the HCl molecule.

The preparation of diaziridine **1a** ended with the decrease in the reaction volume since product density was higher than that of the initial reagents. That is why the reaction at high pressure was considered to be most suitable for accelerating the synthesis of diaziridine **1a** from *N*-chloroethylamines **3a**. It should be mentioned that common acceleration of the reaction rate by increasing the temperature is not suitable. It gives rise to side reactions; the key of which is the decomposition of *N*-chloroethylamine **3**a. All experiments were carried out using the reaction block shown in Figure 2.

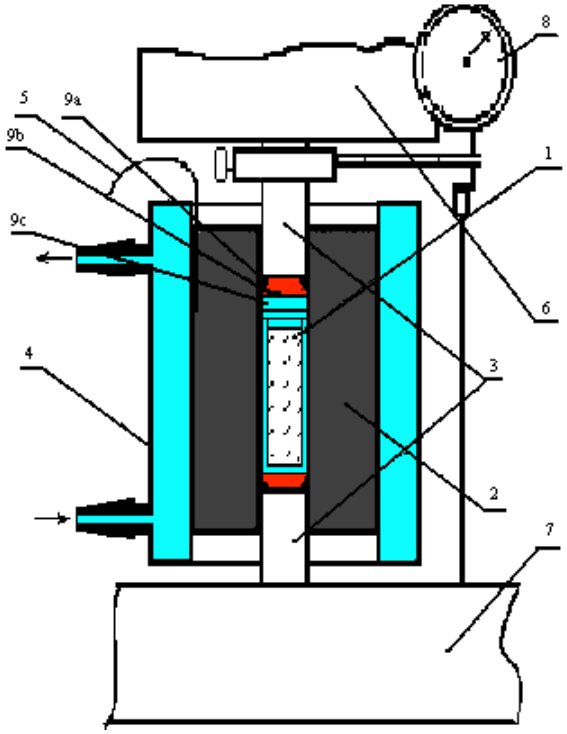


Figure 2. Reaction block for performing chemical reactions at high pressures: 1- Teflon ampoule for reaction mixture; 2- High-pressure block of constructional steel with hardness HRC 40-42; 3-Steel pistons with hardness HRC 58-60; 4- thermostatic jacket; 5- thermocouple; 6-Press plunger; 7-Press frame support; 8- Micrometer. Reaction volume compression comprise from: an anti-extrusion steel ring - 9a, a copper disk - 9b, a Teflon disk - 9c.

Reaction vessels were 12.5 cm^3 Teflon ampoules placed on corresponding high volume block. The thermostatic jacket was put on the high-pressure block and cooled with water from thermostat. A set of packing gaskets was used as hermetic seal for the reaction: an anti-extrusion steel ring with the triangular section and a Teflon-4 annealed copper disk. With pressure increasing, the deformation of the packing gaskets occurred, in turn, resulting in reaction volume impermeability.

Pressure [P] was calculated by the equation: $P = P_{man} * S_r/S_{p,}$ where P_{man} , P – pressure in the press cylinder and reaction block, S_r, S_p - piston face and press plunger correspondingly.

The reaction mixture consisting of the solution of *N*-chloroethylamine **3**a and ethylamine **2**a in $CHCl_3$ and molar ratio 1:3, K_2CO_3 was added with 0.5 mole and a small water amount (~1-2% by volume) and kept at 20-22°C under the adjusted pressure and pre-given time. Then the reaction mixture was analyzed by ^1H NMR spectroscopy. All experiment results are shown in Fig. 3. Consumption of *N*-chloroethylamine **3a** conforms to second order reaction in all the cases (see Figure 3). However, as the pressure increases accumulation of diaziridine **1a** deflects from the second order reaction which is related to the side reaction of polymerization.

According to Figure 3 almost complete conversion of *N*-chloroethylamine **3a** at 300 MPa has been achieved after over 50 h. The yield of diaziridine **1a** was above 90%. At 500 MPa the reaction completed after 10 h with the same yield. When the pressure increased further up to 700 MPa, the polymerization products were predominantly afforded as well as diaziridine **1a** in low yield.

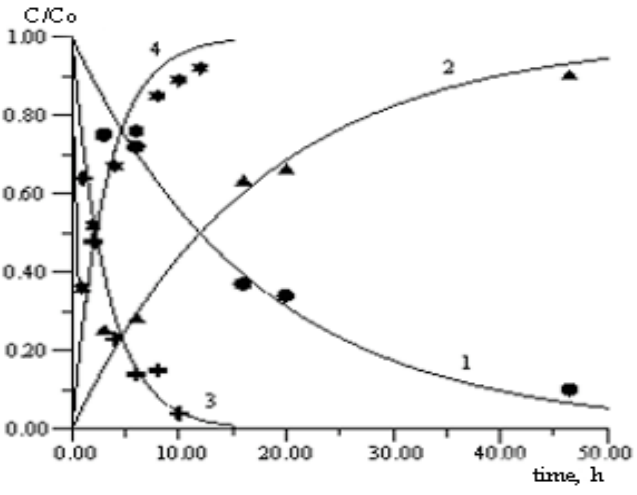


Figure 3. Kinetic curves of the diaziridine **1a** formation from *N*-chloroethylamine **3**a at high pressure. Curves 1 and 3 correspond to consumption of *N*-chloroethylamine **3**a. Curves 2 and 4 correspond to accumulation of diaziridine **1a**. Curves 1 and 2 were recorded at 300 MPa. Curves 3 and 4 were recorded at 500 MPa.

A correlation between the reaction rate constant of the diaziridine **1a** accumulation and pressure is shown in Fig. 4. The reaction constant was estimated at the initial slope of the kinetic curves (see Figure 3). The curve in Figure 4 was estimated using the equation $k = k_0 \exp\frac{-\Delta V^{\neq} P}{RT}$ where P – pressure, T – temperature, R – gas constant, $\Delta V^{\neq}$ = -15 cm^3/mole – activation volume. It can be easily seen that $\Delta V^{\neq}$ = -15 cm^3/mole found for the reaction of the diaziridine **1a** formation is located in the area of the value $\Delta V^{\neq}$ which is typical for the condensation reaction.

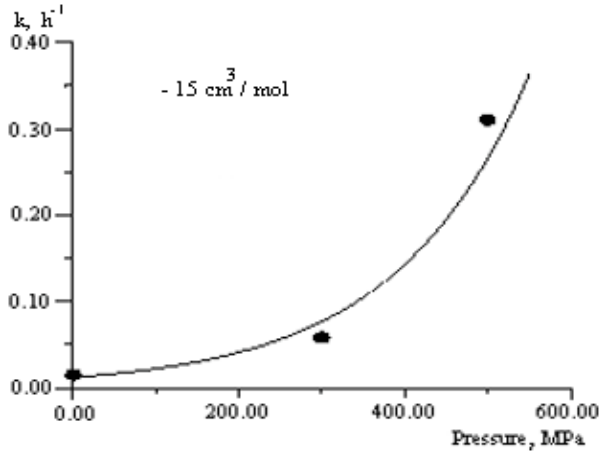


Figure 4. A curve of correlation between reaction rate constant of diaziridine **1a** formation from *N*-chloroethylamine **3**a and pressure.

The temperature and reagents ratio has significant importance for the success of this reaction. The decrease in the temperature down to 15° C at 500 MPa proved to be a 1.3-fold increase in the reaction time ($E_{act.}$~ 40 Kdg/mole). The decrease in the temperature down to 10° C at 700 MPa significantly diminishes the side processes of the polymer formation, although the yield of diaziridine **1a** obtained at other pressures is not reached. To optimize the process of the diaziridine **1a** synthesis we examined the influence of the molar ratios *N*-chloroethylamine **3a**: ethylamine **2a**, K_2CO_3:*N*-chloroethylamine **3a** as well as of the added water amount. As a result of all the investigations it was found that the optimal conditions for the preparation of 1,2-diethy-3-methyldiaziridine **1a** from *N*-chloroethylamine **3a** were: pressure 500 MPa, temperature 15° C, molar ratio of the compounds **3a:2a** = 2.5:1, K_2CO_3 amount – 0.5 mole per 1 mole of *N*-chloroethylamine **3a**, 2% (by volume) of water and reaction time 12-13 hours. In these conditions, the yield of diaziridine **1a** was 95% and the formation of the side products was not actually observed. The formation of the side products is evidently associated with polymerization of imines formed at the first steps of the process because independently synthesized diaziridine **1a** did not change in the reaction conditions.

A few other N-chloroalkylamines **3b-f** were used in the analogous reaction under the identified conditions. The conversion of initial compounds **3b-f** was also controlled by ^{1}H NMR spectroscopy. In all the instants corresponding diaziridines **1b-f** were prepared in good yields (Scheme 2, Table 1). It is interesting to note that reaction time remarkably increased at electron withdrawing fragments entering the substituents of initial N-chloroalkylamines similar to the same reactions at atmospheric pressure.

Scheme 2

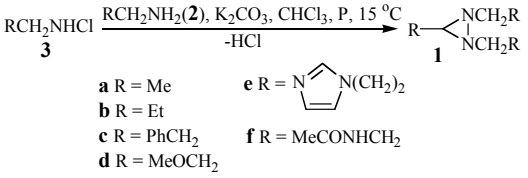


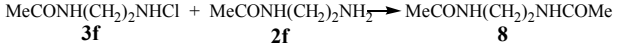
Table 1

The time of reactions and yields of 1,2,3-trialkyldiaziridines **1a-f** from N-chloroalkylamines **3a-f** at temperature 15 °C and pressure 500 MPa

Initial *N*-chloroalkylamines **3**	Time of reaction h	Yield of diaziridines **1** (%)
EtNHCl **3a**	12-13	**1**a (95)
PrNHCl **3b**	12-13	**1b** (84)
$PhCH_2CH_2NHCl$ **3c**	46-48	**1c** (82)
$MeOCH_2CH_2NHCl$ **3d**	46-48	**1d** (91)
N N(CH2)3NHCl **3e**	35-36	**1e** (78)
$MeCONHCH_2CH_2NHCl$ **3f**	46-48	**1f** (57)

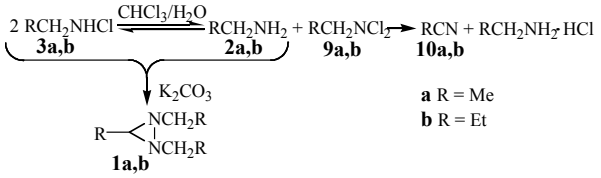
As seen from Table 1, the yields of final diaziridines **1** are rather high, except for compound **1f**. The decrease in the yield of diaziridine **1f** evidently related to the reacylation reaction which resulted in 1,2-diacetylethylenediamine **8** (Scheme 3). The latter was isolated from reaction of the *N*-chloroamine **3f** and characterized (Table 1).

Scheme 3



To extend possible approaches to the diaziridine synthesis on a basis of the *N*-chloroalkylamines **3** transformation we studied the behavior of compounds **3** (on the example of **3a,b**) in the identified optimal conditions though without the addition of corresponding alkylamines **2a,b**. It was found that in these cases 1,2,3-trialkyldiaziridines **1a,b** were generated as well, however in lower yields (47-55%). The success of this reaction depends on the known capacity of *N*-chloroalkylamines **3** to transform into corresponding amines **2** and *N,N*-dichloroalkylamines **9** [22]. Then *N*-chloroalkylamine **3** and alkylamine **2** lead to diaziridines **1** according to Scheme 4. This alternative of the synthesis of diaziridines **1** allows not only obtaining diaziridines **1** in the absence of carbonyl compounds but also saving initial amines through the use of K_2CO_3 as a base. In the absence of K_2CO_3 nitriles **10a,b** were isolated as a result of the transformation of *N,N*-dichloroalkylamines **9a,b** (Scheme 4).

Scheme 4



Therefore two optimal approaches to the synthesis of 1,2,3-trialkyldiaziridines **1** based on the transformation of *N*-chloroalkylamines **3** in the absence of carbonyl compounds at high pressure have been found. The first approach includes the interaction of *N*-chloroalkylamine **3** with an excess of primary aliphatic amine **2** containing the same alkyl substituent in $CHCl_3$ in the presence of 0.5 mole of K_2CO_3 and a small water amount at 500 MPa and 15° C. The second approach is based on the same reaction but with using 1 mole of K_2CO_3 and without adding primary aliphatic amine **2**. The developed methods are especially attractive where appropriate aldehydes are hardly available.

The kinetic studies of the synthesis of 1,2,3-trialkyldiaziridines **1** from *N*-chloroalkylamines **3** at high pressure (on the example of 1,2-diethyl-3-methyldiaziridine **1a)** have revealed that these reactions conform to the second order law at all pressures. Assumingly, the limiting step of the process is the bimolecular interaction of *N*-chloroalkylamine **3** with primary aliphatic amine **2** followed by the elimination of the HCl molecule. As a whole, using the synthesis of 1,2,3-trialkyldiaziridines **1** as an example, has been shown a unique possibility of employing high pressure to stimulate chemical processes, effectiveness of which can not be enhanced through heating due to side reactions.

EXPERIMENTAL

Elemental analysis was performed by the CHN Analyzer Perkin-Elmer 2400. The ir spectra (ν, cm^{-1}) were measured using a UR-20 spectrometer. Mass spectra were measured using a Finnigan MAT INCOS-50 instrument. All of the nmr spectra were recorded using a Bruker AM-300 spectrometer at 300 MHz for ^{1}H and 75.47 MHz for ^{13}C Spectra in $CDCl_3$. The chemical shifts are shown in δ and are expressed relative to the chemical shifts for the $CDCl_3$ (7.27 ppm and 77.08 ppm for ^{1}H and ^{13}C nmr, respectively). Analytical thin-layer chromatography (TLC) was conducted on silica gel plates (Silufol UV-254). New compounds were isolated on Kieselgel 0.060-0200 mm, 60 A (ACROS).

General procedure for the synthesis of 1,2,3-trialkyldiaziridines 1 from *N*-chloroalkylamines 3 and corresponding alkylamines 2 in the presence of K_2CO_3 under high pressure. Solution of *tert*-BuOCl (0.64 ml, 5.7 mmol) in 0.5 ml of chloroform was added dropwise to a solution of 20 mmol of amine **2** in 10 ml of chloroform at intensive stirring and temperature 0-5 °C. The reaction mixture, containing the mixture of 14.3 mmol of amine **2** and 5.7 mmol of *N*-chloroalkylamine **3**, was put in fluoroplastic reaction ampoule with volume 12,5 cm^3, potassium carbonate (0.41 g, 3 mmol) and two drops of water were added. Then chloroform was added to fill whole volume of the ampoule and the latter was closed with cover. The reaction ampoule was put in the barostate (see Fig. 2) and kept at 500 MPa, temperature 15 °C during 12-13 hours for compounds **3a,b**, 35-36 hours for compound **3e** and 46-48 hours for compounds **3c,d,f**. The pressure was decreased to normal value, the ampoule was elicited from the barostate, the precipitate was filtered, washed with 5 ml of chloroform and a solvent was evaporated. The diaziridnes **1a** and **1b** were distilled in vacuum and compounds **1c-f** were isolated by chromatography on Kieselgel 0.060-0.200 mm, 60Å.

Synthesis of 1,2,3-Trialkyldiaziridines 1a,b from *N*-chloroalkylamines 3a,b and K_2CO_3 under high pressure (general procedure). Solution of *tert*-BuOCl (1.12 ml, 10 mmol) in 1.0 ml of chloroform was added dropwise to solution of 10 mmol of amines **2a** or **2b** in 8 ml of chloroform at stirring and temperature 0-5 °C. The reaction mixture, containing of 10 mmol of *N*-chloroamines **3a** or **3b**, was put in fluoroplastic reaction ampoule with volume 12.5 cm^3, potassium carbonate (1.38 g, 10 mmol) and two drops of water were added. Then chloroform was added to fill whole volume of the ampoule and the latter was closed with cover. The reaction ampoule was put in the barostate (see Fig. 2) and was kept at 500 MPa and temperature 15 °C during 12-13 hours. The pressure was decreased to normal value, the ampoule was elicited from the barostate, the precipitate was filtered, washed with 5 ml of chloroform and a solvent was evaporated. The diaziridnes **1a** and **1b** were distilled in vacuum.

1,2-Diethyl-3-methyldiaziridine 1a: 95% yield, bp. 43-44 °C (20 Torr), (lit[3] 43-45 °C (20 Torr)); MS m/z (I%): 113 (M^+ -1, 37%), 72 (M^+ - NEt, 68%), 42 (NEt, 100%).

1,2-Di-*n*-propyl-3-ethyldiaziridine 1b: 84% yield, bp. 71-73 °C (12 Torr), (lit[3] 71-73.5 °C (12 Torr)).

1,2-Bis(2-phenylethyl)-3-(phenylmethyl)diaziridine 1c. 82% yield, nondistilled oil, n_D^{20}1.5722, R_f 0.39 (hexane:ethyl acetate 4:1 (v/v)), ir: 3028, 3004, 2932, 2860, 2846, 1668, 1604, 1584, 1496, 1456, 1360, 1244, 1180, 1084, 1032, 984, 912, 732, 700, 644 cm^{-1}; ^{1}H nmr: δ 2.6-3.1 (m, 11H, PhCH_2, N-CH_2, $CH_{diaz.\ ring}$), 7.32 (m, 15H, Ph); ^{13}C nmr: δ 126.12 (PhCH_2CH_2), 126.20 (PhCH_2CH_2), 126.65 (PhCH_2CHdiaz. ring), 54.53 (NCH_2), 62.79 (NCH_2), 66.38 ($C_{diaz.ring}$), 126.12, 126.2, 126.65, 127.92, 128.06, 128.40, 128.45, 128.70, 128.89, 129.15 (Ph); MS m/z: (I%): 251 (M^+ - CH_2CH_2Ph, 52%), 105 (CH_2CH_2Ph, 100%), 91 (PhCH_2, 67%), 77 (Ph, 38%). *Anal.* Calcd for $C_{24}H_{26}N_2$ (342.52): C, 84.15; H, 7.67; N, 8.18. Found: C, 84.32; H, 7.52; N, 7.96.

1,2-Bis(2-metoxyethyl)-3-(methoxymethyl)diaziridine 1d. 91% **y**ield, nondistilled oil, n_D^{20}1.4468, R_f 0.37 (1.7% NH_3 in $CHCl_3$), ir: 2980, 2928, 2880, 2816, 2756, 1684, 1528, 1456, 1348, 1320, 1284, 1236, 1200, 1120, 1024, 964, 932, 848, 756 cm^{-1}; ^{1}H nmr: δ 2.47, 2.53 (dt, 1H, NCH, ^2J = 14.3 Hz, ^3J = 3.3 Hz, Δν = 116.6 Hz), 2.57, 2.62 (dt, 1H, NCH, ^2J = 13.2 Hz, ^3J = 4.4 Hz, Δν = 85.8 Hz), 2.87 (m, 2H, NCH), 3.38 (s, 3H, OMe), 3.4 (s, 6H, OMe), 3,52 (m, $CH_{diazir.\ ring.}$), 3.62 (m, 6H, CH_2O) ; ^{13}C nmr: (δ, $J_{13C\text{-}1H}$): 52.3 (t, O$CH_2C_{diaz.\ ring}$ ^1J = 135 Hz), 59.04 (q, OMe, ^1J = 141 Hz), 59.22 (q, OMe, ^1J = 135 Hz), 60.38 (t, NCH_2, ^1J = 140 Hz), 63.07 (t, $CH_{diaz.\ ring}$, ^1J = 80 Hz), 68.95 (t, NCH_2, ^1J = 138 Hz), 71.14, 71.59 (OMe), MS m/z: (I%): 159 (M^+ - $MeOCH_2$, 17.5%), 59 ($MeOCH_2CH_2$, 53%), 45 ($MeOCH_2$, 100%). *Anal.* Calcd for $C_9H_{20}N_2O_3$ (204.31): C, 52.90; H, 9.89; N, 13.71. Found: C, 52.75; H, 10.10; N, 14.02.

1,2-Bis[3-(imidazol-1-yl)propyl]-3-[2(imidazol-1-yl)ethyl]-diaziridine 1e. 78% yield, nondisstilled oil, n_D^{20}1.5768, R_f 0.23 (5% NH_3 in $CHCl_3$:MeOH 60:1 (v/v)), ir: 3108, 2944, 2856, 1672, 1508, 1452, 1396, 1360, 1284, 1232, 1112, 1080, 1032, 908, 820, 736, 664, 624 cm^{-1}; ^{1}H nmr: δ 1.85 (m, 6H, $CH_2CH_2CH_2$ + $CH_2C_{diazir.\ ring}$, ^3J = 7 Hz, Δν = 61 Hz), 2.04 (m, 2H, NCH, ^3J = 6.5 Hz, $\Delta\nu^1$ = 61 Hz, $\Delta\nu^2$ = 110 Hz), 2.23 (m, 1H, NCH, ^3J = 6.23 Hz, $\Delta\nu^1$ = 61 Hz), 2.32 (m, 1H, $CH_{diazir.\ ring}$), 2.40 (m, 1H, NCH, ^3J = 6.5 Hz, $\Delta\nu^2$ = 110 Hz), 4.0 (m, 6H, CH_2-$N_{imidaz.\ ring}$), 6.84, 6.85, 6.87 (three s, $C^4H_{imidaz.\ ring}$), 6.98, 6.99, 7.02 (three s, $C^5H_{imidaz.\ ring}$), 7.4, 7.41, 7.43 (three s, $C^2H_{imidaz.\ ring}$); ^{13}C nmr: δ: 28.19, 30.27, 30.67 (C-CH_2-C), 44.47, 44.60 (N-CH_2), 49.01, 57.10, 57.64 (CH_2-$N_{imidaz.\ ring}$), 62.55 ($C_{diaz.\ ring}$), 118.79 ($C^4_{imidaz.\ ring}$), 129.41, 129.66, 130.04 ($C^5_{imidaz.\ ring}$), 139.98, 137.19, 137.24 ($C^2_{imidaz.\ ring}$); MS m/z (I%): 232 (M^+-imid.ring$CH_2CH_2CH_2$N, 23%), 123 (imid.ring$CH_2CH_2CH_2$N, 51%), 107 (imid.ring$CH_2CH_2CH_2$, 92%), 96 (imid.ringCH_2CH_2, 72%), 82 (imid.ringCH_2, 100%), 68 (imid.ring, 98%). *Anal.* Calcd for $C_{18}H_{26}N_8$ (354.52): C, 60.98; H, 7.41; N, 31.61. Found: C, 60.75; H, 7.62; N, 14.35.

1,2- Bis(2-acetamidoethyl)-3-(acetamidomethyl)diaziridine 1f. 57% yield, nondistilled oil, R_f 0.41 (5% NH_3 in $CHCl_3$:MeOH 15:4 (v/v)), ^{1}H nmr: δ 2.02, 2.04, 2.07 (three s, 9H, Me), 2.62 (m, 4H, NCH_2), 2.78 (t, 1H, $CH_{diaz.\ ring}$, ^3J = 5.5 Hz), 3.48 (m, 6H, CON-CH_2), 6.28, 6.38, 7.15 (three br. s, NH); ^{13}C nmr: δ: 23.09, 23.28, 23.37 (Me), 36.83, 38.45, 39.15 ($NHCH_2$), 51.58, 60.26 ($CH_2N_{diaz.\ ring}$), 63.36 ($C_{diaz.\ ring}$), 170.78, 170.86, 171.11 (CO). *Anal.* Calcd for $C_{12}H_{23}N_5O_3$ (285.40): C, 50.50; H, 8.14; N, 24.54. Found: C, 50.25; H, 8.24; N 24,24.

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